Fluctuation effects on the thermal expansion of the incommensurate crystal Sn2P2Se6

Maior, M.M.; Loosdrecht, P.H.M. van; Kempen, H. van; Rasing, Th.; Molnar, S.B.; Motrij, S.F.

Published in:
Journal of Physics%3A Condensed Matter

DOI:
10.1088/0953-8984/5/33/011

Publication date:
1993

J. Phys.: Condens. Matter 5 (1993) 6023–6028. Printed in the UK

Fluctuation effects on the thermal expansion of the incommensurate crystal $Sn_2P_2Se_6$

M M Maior†‡, P H M van Loosdrecht‡, H van Kempen‡, Th Rasing‡, S B Molnar† and S F Motrij†

† Institute of Physics and Chemistry of Solid State, Uzhgorod State University, 294000 Uzhgorod, Ukraine

‡ Research Institute for Materials, University of Nijmegen, Toernooiveld, NL-6525 ED Nijmegen, The Netherlands

Received 28 May 1993

Abstract. The paraelectric–incommensurate and the incommensurate–commensurate phase transitions of the proper ferroelectric crystal $Sn_2P_2Se_6$ are studied by thermal expansion measurement on crystals grown by two different techniques. For vapour-transport grown crystals the observed deviation around T_i from the Landau theory can be described by a small fluctuation correction, whereas for Bridgemann-method grown crystals this deviation is most likely to be due to random local field-type defects. For both types of crystals in the low-temperature region of the incommensurate phase an additional contribution to the spontaneous deformation above the Landau part has been revealed.

1. Introduction

$Sn_2P_2Se_6$ is one of the few proper ferroelectrics that undergoes an incommensurate (IC) phase transition. The temperature range of the IC phase in this crystal is restricted to the temperature interval $T_c \approx 193\,K < T < T_i \approx 220\,K$. Above T_i $Sn_2P_2Se_6$ is in the paraelectric phase with the centrosymmetric space group $P2_1/c$. Below the lock-in phase transition the crystal is ferroelectric with the space group Pc. The IC phase is characterized by a modulation wavevector q_z that varies with temperature between $0.08c^*$ and $0.071c^*$ [1].

The critical behaviour in the vicinity of the phase transition in $Sn_2P_2Se_6$ has been studied by birefringence measurements [1]. The observed deviation from a mean-field behaviour near the IC phase transition is usually attributed to order parameter fluctuations or defects. Remarkable deviations occur in some crystals in the low-temperature part of the IC phase. In particular, a marked increase in the mean-squared order parameter while approaching the lock-in phase transition has been revealed by birefringence measurements in thiourea [2] and $Sn_2P_2Se_6$ [3]. This effect was interpreted as a contribution of higher-order harmonics to the average square of the order parameter.

In this paper we report thermal expansion experiments on $Sn_2P_2Se_6$. The spontaneous deformation arising in the ferroelectric phase as well as in the IC phase has an electrostrictional character; it is a square function of the spontaneous polarization. The order parameter contribution, (δ) to the thermal expansion ($\Delta l/l_0$) can be described by the formula

$$\delta_j = Q_{ji}\langle P_i^2 \rangle \tag{1}$$

0953-8984/93/336023+06$07.50

where $\langle P_i^2 \rangle$ is the mean-square of the order parameter and Q_{ij} is the electrostrictional coefficient. Thus, dilatometric measurement can serve as a convenient method for the investigation of the IC phase. This method provides sufficiently high accuracy to define the critical exponent α, corresponding to the temperature behaviour of the heat capacity.

2. Experiment

The temperature dependence of the thermal expansion was measured using a capacitance dilatometer with a resolution of about 1 nm. The measurements were performed in a flow cryostat in a quasi-static regime upon cooling with a temperature variation rate of $0.5\,\mathrm{K\,min^{-1}}$. For the experiments $Sn_2P_2Se_6$ crystals grown by vapour transport and the Bridgemann method were employed. Because the most pronounced anomalies of the thermal expansion in this kind of materials are observed along the (100) and (010) axes [4], we have carried out the measurements for these directions. Samples in the form of parallelepipeds with linear dimensions of about 5 mm were used.

Qualitatively, the temperature dependences of the thermal expansion for both directions are found to be similar. Therefore only data corresponding to the (010) direction are presented for the analysis. The samples were mounted inside a temperature-controlled copper housing. To evaluate the data one needs to subtract the spontaneous deformation related to the phase transition from the total temperature dependence of $\Delta l/l_0$. The rather wide temperature region from 290 K to approximately 235 K, with a linear temperature dependence of $\Delta l/l_0$, allows us to make a reliable subtraction of the background by extrapolation of the high-temperature behaviour.

3. Discussion

3.1. The paraelectric–incommensurate phase transition

Figure 1 shows the spontaneous deformation obtained after the subtraction of the background for $Sn_2P_2Se_6$ crystals grown by the two different methods. The $\delta(T)$ curves are continuous at T_i and exhibit a non-linear temperature dependence below and above T_i. Figure 2 presents the temperature dependence of the derivative of $\delta(T)$. These curves were obtained after smoothing the experimental data in figure 1. As can be seen from the figures $k = \mathrm{d}\delta/\mathrm{d}T$ has a maximum near T_i. It should be mentioned that the maximum for the Bridgemann-type crystal is broader than for the vapour-transport-type one. Moreover the amplitude of the tail of $k(T)$ above the maximum is larger for the first than for the latter. The linear temperature dependence of δ in part of the IC phase (figure 1(*a*) and (*b*) is an indication of the simple Landau-type behaviour. The broken lines show the extrapolation of this linear behaviour to a temperature corresponding to the 'virtual' phase transition in the Landau approximation. The corresponding jumps of the Landau-type are shown by the broken line in figure 2.

We now discuss in detail the observed deviations from the Landau behaviour. In the vapour-transport-type crystal this deviation is symmetric around T_i (figure 2(*a*)). At the same time in the Bridgemann-type crystal the deviation has a pronounced asymmetric character (figure 2(*b*)). The excess part over the Landau jump can be caused by order parameter fluctuations or defects. Analogously to the birefringence effect [5], the order parameter

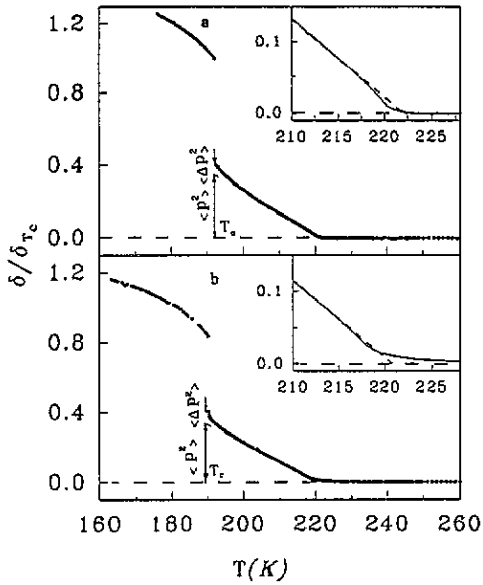

Figure 1. Temperature dependence of the normalized spontaneous deformation for $Sn_2P_2Se_6$ crystals grown: (*a*) by the vapour-transport technique, and (*b*) by the Bridgemann method along the (010) axis. The broken lines correspond to the extrapolation of the linear region inside the IC phase to the high and low temperatures (simple Landau-type behaviour). The inserts show the spontaneous deformation behaviour close to T_i.

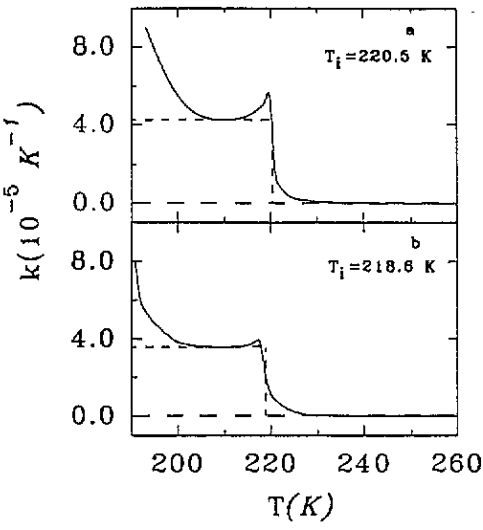

Figure 2. Temperature dependences of the derivatives of the spontaneous deformation corresponding to (*a*) the vapour-transport-type, and (*b*) the Bridgemann-type of $Sn_2P_2Se_6$ crystals.

fluctuations give a contribution to the thermal expansion coefficient in the vicinity of the IC phase transition that can be described by the following relations:

$$\begin{aligned} k^+ &= k_b + \lambda^+ \tau^{-0.5} \qquad \text{for } \tau > 0 \\ k^- &= k_b + k_L + \lambda^- \tau^{-0.5} \qquad \text{for } \tau < 0 \end{aligned} \tag{2}$$

where k_b is the background, k_L is the Landau jump, $\tau = |T_i - T|/T_i$ and $\lambda^-/\lambda^+ = \sqrt{2}$. The validity region of the fluctuation corrections, $\lambda^{\pm}\tau^{-0.5}$, to the Landau theory is defined by the Ginzburg–Levanyuk criterion. For the $Sn_2P_2Se_6$ crystals this was estimated on the basis of the heat capacity data [1], and yields $\tau \approx 10^{-2}$, which corresponds to approximately 4 K. It should be noted that this estimate is very rough and only gives an order of magnitude. The log–log plot of k against $(T_i - T)$ for the crystal of the vapour-transport-type gives an exponent of 0.53 ± 0.05 above T_i, while below T_i this exponent is 0.54 ± 0.05 for $0.9 < (T_i - T) < 10$ K. T_i was chosen at the midpoint of the $k(T)$ jump. For the ratio of λ^-/λ^+, we find the value 1.3. In the immediate vicinity of T_i the fluctuation correction to the Landau theory is not valid any more. The thermal expansion coefficient should exhibit a sharp maximum at T_i and the critical exponent α should be small and negative [5]. We observed no such behaviour. Most likely this is due to the smearing of the phase transition by defects.

The log–log plot of δ against $(T_i - T)$ in the vapour-transport-type crystal in the temperature region between $T_i - 0.9$ K and $T_i - 6$ gives an exponent of 0.72 ± 0.03 K.

One can believe this temperature range to correspond to the non-critical region, where the deviation from the 'classical' Landau theory ($2\beta = 1$) can be accounted for by the fluctuation correction [5]. The fact that the exponent for the temperature dependence of k found for this temperature region (see above) is very close to the value corresponding to the fluctuation correction (0.5) is an argument in favour of this conclusion. Thus, the effective exponent 0.72 ± 0.03 obtained below T_i, can be attributed to the alteration of the Landau behaviour by the fluctuation correction as well as to the renormalization of the phase transition temperature (see figure 1) by the order parameter fluctuations [5]. One can therefore conclude that, except for the region immediately adjacent to T_i, the thermal expansion behaviour at the paraelectric–IC phase transition in $Sn_2P_2Se_6$ can be described in the framework of the Landau theory including the fluctuation correction.

In the case of the Bridgemann-type crystal the behaviour of $k(T)$ above T_i +2 K obeys a power law with an exponent of 1.05 ± 0.05. The temperature dependence of k below T_i shows a broad maximum (figure 2). Because T_i is less sharply defined, it is impossible to make any reliable power law fit in this region. It is well known that the quality of the crystals grown by the Bridgemann method is worse than that of the crystals obtained by the vapour-transport technique. As is known from [6], a significant influence on the IC phase transition is expected from the random-field-type defects. This kind of defect breaks-down the long-range order in the IC phase, and consequently they can be responsible for the smearing observed in the Bridgemann-type crystals. According to theory [5] random local-temperature defects do not change the critical behaviour, whereas the presence of the random local field defects leads to an exponent $\alpha = 1.5$. The value of 1.05 for α, which is higher relative to $\alpha = 0.5$, corresponding to the fluctuation correction to the Landau theory, is an argument in favour of the random-field-type defects. As to the nature of the defects, in the case of the sulphur compound, $Sn_2P_2S_6$ [7], it is found to be associated with deviation from the stoichiometry in the cation sublattice (for the crystals grown by the Bridgemann method). Moreover, the defects of this type are responsible for the internal electric field arising during the process of spontaneous polarization screening. This fact is also a strong argument in favour of the random local-field-type defects. The temperatures of both phase transitions in Bridgemann crystals are found to be lower than in the vapour-transport crystals. This shift of the phase transitions to lower temperatures is probably also due to the influence of defects.

3.2. The incommensurate–commensurate phase transition

Figure 1 shows that in crystals of both types δ shows a linear behaviour in a temperature region extending over about 10 K inside the IC phase. On approaching T_c, δ exhibits a surprising increase, deviating from Landau behaviour. At the lock-in phase transition δ shows a very distinct jump upwards within a very narrow temperature region ($\Delta T \approx 0.2$ K). One of the reasons for this observed deviation may be the appearance of higher-order harmonics in the incommensurate distortion, or in other words the transformation of a sinusoidal modulation into the soliton regime. A measure for this contribution can be estimated from the ratio $\langle \Delta P^2 \rangle / \langle P^2 \rangle$. Here $\langle \Delta P^2 \rangle$ indicates the additional contribution above the linear extrapolation and $\langle P^2 \rangle$ the contribution corresponding to the Landau theory. At T_c (figure 1) this ratio is found to be equal to 0.17 and 0.19 for vapour transport and Bridgemann crystals, respectively. If this contribution is supposed to be connected with the higher-order harmonics, the ratio of the effective amplitude of this contribution to the amplitude of the fundamental IC modulation, assuming their phases to be the same, is $\Delta P / P_{1q} = 0.41$ and 0.44, respectively. It is known that in crystals with an IC phase without the Lifshitz invariant, as for the proper ferroelectric $Sn_2P_2Se_6$, the higher-order harmonics

remain small throughout the whole IC phase. In particular, the ratio of the amplitudes of the third and the fundamental harmonic, P_{3q}/P_{1q}, is 0.026 [8], while the higher-order harmonics are negligibly small. From the above estimate it follows that the observed increase cannot be explained by contribution of higher-order harmonics. This conclusion is supported by the results of an x-ray investigation of the IC phase in $Sn_2P_2Se_6$ that did not show any higher-order harmonics within an accuracy of 5% [9]. Similar behaviour has also been observed in temperature dependence of the birefringence in $NaNO_2$ [10]. The temperature region of the IC phase in this crystal is so small (1.5 K) that one would not expect that higher-order harmonics can play an important part. Additional indication of a non-solitonic behaviour in the $Sn_2P_2Se_6$ crystal is the absence of dielectric dispersion in the frequency range corresponding to the soliton relaxation as well as the absence of soliton-like behaviour of the dielectric susceptibility under influence of bias field (reduction of ϵ due to suppression of the dielectric response of the soliton structure).

It should be noted that in the case of crystals without the Lifshitz invariant the soliton-type solution for the order parameter distribution has been obtained [11]. However, in that case the phase transition to the commensurate phase should be continuous. This is contrary to the experimentally observed situation in $Sn_2P_2Se_6$, which exhibits a strong first-order phase transition.

It is well known that IC phases are highly sensitive to defects. In some materials a so-called chaotic state has been observed in the low-temperature part of the IC phase, which is ascribed to the influence of the defects [12]. Such a state is characterized by the coexistence of the IC phase with inclusions of the commensurate phase. This can lead to a deviation from Landau theory. However as can be seen from figure 1(*a*) and (*b*), the temperature behaviour of the spontaneous deformation as well as its derivative does not differ significantly in both types of crystals. The only difference is found in the temperature region of about 1 K above T_c, where the Bridgemann type crystal shows a much sharper increase in $\delta(T)$. Due to the defects this precursor effect takes place in close vicinity of the first-order phase transition. However, the excess enhancement of the spontaneous deformation in the observed wide temperature region (figure 1) cannot be related to the influence of defects.

Due to the $\gamma P^2(\nabla P)^2$ term in the thermodynamic potential the wavevector of the IC modulation becomes temperature dependent:

$$q^2 = q_i^2 - \gamma P_q^2/2\eta \tag{3}$$

where (in notation of [8]) q_i is the wavevector at T_i and η is the coefficient in the quadratic term, $1/2(\alpha + \delta q^2 + \eta q^4)P_q^2$, in the thermodynamic potential. The character of the temperature dependence of the wavevector [9] and spontaneous deformation in $Sn_2P_2Se_6$ indicates that (3) holds, at least qualitatively. This shows that the one-harmonic approximation should be valid up to T_c. Note that the amplitude of the modulation at T_c (for the vapour-transport-type crystal) represents $0.9P_0$, where P_0 is spontaneous polarization at T_c in the ferroelectric phase (see figure 1). Therefore one can conclude that the amplitude of the polarization at the phase transition to the ferroelectric phase does not change very much. A deviation from the classical behaviour of the thermodynamic quantities in the vicinity of the lock-in phase transition has been observed in some improper ferroelectrics. This feature is attributed to order parameter fluctuations [12, 13]. As far as we know there is no correct theory considering the behaviour of the incommensurate modulation in the proper ferroelectrics in the vicinity of the lock-in phase transition. Thus, the question of what is the nature of the additional contribution to the spontaneous deformation remains open. To clarify this problem additional experimental (in particular structural) and theoretical investigations are required.

4. Conclusion

The paraelectric–incommensurate–commensurate sequence of phase transitions in $Sn_2P_2Se_6$ was studied by dilatometry, using single crystals grown by vapour transport and by the Bridgemann method. For the high-quality vapour-transport crystals the behaviour near T_i of the spontaneous deformation which is a square function of $\langle P_i \rangle$, as well as the thermal expansion coefficient, can be described by Landau theory with a small fluctuation correction. The deviation from Landau theory found for the Bridgemann-grown crystals results primarily from the presence of local-field-type defects. In the low-temperature part of the incommensurate phase an additional contribution to the spontaneous deformation above the Landau part has been found for both crystal types. This effect cannot be a consequence of the higher harmonics in the IC modulation or defects influence. Its nature remains an open question.

Acknowledgments

One of us (MMM) would like to express his thanks to the staff of the Research Institute for Materials of the University of Nijmegen for their hospitality and assistance and the Dutch and former Soviet Union governments for financial support through a cultural exchange program.

References

[1] Vysochanskii Yu M, Maior M M, Rizak V M, Slivka V Yu and Khoma M M 1989 *Sov. Phys.–JETP* **68** 782–7
[2] Farny R, Schafer F J and Kleemann W 1990 *Ferroelectrics* **105** 255–60
[3] Vysochanskii Yu M, Motrij S F, Perechinskii S I, Rizak V M, Rizak I M and Slivka V Yu 1991 *Ukrainsii Fiz. Zh.* **36** 728–31
[4] Maior M M, Koperles B M, Savchenko B A, Gurzan M I, Morozova O V and Korda N F 1983 *Sov. Phys.–Solid State* **25** 117–22
[5] Ivanov N R, Levanyuk L P, Minyukov S A, Kroupa G and Fousek G 1990 *J. Phys.: Condens. Matter* **2** 577–86
[6] Levanyuk A P and Sigov A S 1990 *Defects and Structural Phase Transitions* (New York: Gordon and Breach) p 220
[7] Maior M M, Molnar S B, Vysochanskii Yu M, Potorii M V and Pritz I P 1993 *Fiz. Tver. Tela* at press
[8] Ema K, Hamano K and Levanyuk A P 1990 *J. Phys. Soc. Japan* **59** 1438–50
[9] Parsamian T K, Khasanov S S and Shektman V Sh 1987 *Fiz. Tver. Tela* **29** 1665–8
[10] Bianchi U, Kleemann W and Sommer D 1991 *Phase Transitions* **36** 145–53
[11] Golovko V A 1988 *Zh. Eksp. Teor. Fiz.* **94** 182–97
[12] Prelovsek P and Blinc R 1984 *J. Phys. C: Solid State Phys.* **17** 577–8
[13] Natterman T 1980 *J. Phys. C: Solid State Phys.* **13** L265–8